Nearly-logarithmic decay of correlations in glass-forming liquids

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Nearly-logarithmic decay of correlations, which was observed for several supercooled liquids in optical-Kerr-effect experiments [G. Hinze et al. Phys. Rev. Lett. 84, 2437 (2000), H. Cang et al. Phys. Rev. Lett. 90, 197401 (2003)], is explained within the mode-coupling theory for ideal glass transitions as manifestation of the β-peak phenomenon. A schematic model, which describes the dynamics by only two correlators, one referring to density fluctuations and the other to the reorientational fluctuations of the molecules, yields for strong rotation-translation coupling response functions in agreement with those measured for benzophenone and Salol for the time interval extending from 2 picoseconds to about 20 and 200 nanoseconds, respectively.

Optical-Kerr-effect (OKE) spectroscopy is a powerful technique for the study of the dynamics of supercooled liquids [1]. The experiment provides a response function $\chi_A(t)$ for times t exceeding a fraction of a picosecond. The function $\chi_A(t)$ is proportional to the negative time derivative of a correlator $\phi_A(t) = \langle A^*(t)A\rangle/\langle|A|^2\rangle$. Here, $\langle\rangle$ denotes canonical averaging, and the probing variable A is the anisotropic part of the dielectric function. The instrumentation was improved recently by application of heterodyne detection. As a result, it was possible to measure $\chi_A(t)$ for times up to 500 nanoseconds, i.e., glassy dynamics was documented for the enormous time interval starting at the end of the transient and extending over more than five orders of magnitude [2]. It was shown that the evolution of the glassy dynamics of Salol upon decreasing the temperature T can be interpreted by the universal formulas derived within the mode-coupling theory of ideal glass transitions (MCT) [1, 2]. The fit values for the various parameters have been found to be consistent with those obtained by other light-scattering techniques [3, 4]. However, the universal formulas do not describe the data for all times outside the transient regime. Rather, if T decreases, there opens a time interval larger than two orders of magnitude, which precedes the interval of validity of the universal formulas. Here, the response for Salol follows closely a $1/t$-law, i.e., the correlator exhibits nearly a logarithmic decay: $\phi_A(t) \propto -\ln(t/\tau)$ [2]. This intriguing feature was observed also for some other van-der-Waals liquids, like benzophenone (BZP). This holds with the reservation that the heretofore unknown relaxation process can be described more adequately by a power law, $\phi_A(t) - f \propto -t^{b'}$, albeit with a rather small exponent b' [5]. Gaining an understanding of the indicated findings is a challenge to all theories aiming to unlock a comprehensive description of liquids. In this Letter, it will be shown that the measured complex relaxation scenario [2, 5] is a generic, though not universal, implication of the standard MCT.

The MCT was proposed as a mathematical model for glassy dynamics [6], whose fascinating features are obtained as implication of bifurcation points of nonlinear equations of motion derived for the density fluctuations. The basic bifurcation is a fold singularity describing a transition from ergodic to non-ergodic behavior if the temperature decreases through a

critical value T_c. Using $\varepsilon = (T_c - T)/T_c$ as a small parameter, the long-time behavior of the correlators can be evaluated by asymptotic expansions [7]. The leading-order formulas establish the universal features of the dynamics. Comparisons of experimental results with these formulas [8] and tests by molecular-dynamics simulation [8, 9] have shown that MCT is a serious candidate for an explanation of glassy dynamics. Nearly-logarithmic decay of correlations was predicted within MCT for states close to bifurcations of the cusp type as can be inferred from Ref. [10] and the papers cited there. It was pointed out [2, 5] that the OKE data might be fitted by the universal results for relaxation near cusp bifurcations. However, one has to vary at least two control parameters in order to approach such singularity. A fit of the OKE data, which only depend on the single control parameter T, would require implausible fine tuning of the coupling coefficients entering the MCT equations. The explanation proposed below is based on the existence of the simple liquid-glass-transition singularity. Our results are valid for response functions of variables A that couple strongly to density fluctuations so that a so-called β-peak can occur in the susceptibility spectra [11, 12].

Let us consider an MCT model describing schematically the density fluctuations by a single correlator $\phi(t)$. It obeys the Zwanzig-Mori equation of motion

$$\partial_t^2\phi(t) + \nu\partial_t\phi(t) + \Omega^2\phi(t) + \Omega^2\int_0^t m(t-t')\partial_{t'}\phi(t')dt' = 0, \tag{1}$$

where Ω and ν are frequencies parameterizing the short-time asymptote, $\phi(t) = 1 - 1/2\,(\Omega t)^2 + 1/6\,\nu\Omega^2 t^3 + O(t^4)$. The kernel $m(t)$, which represents the interactions of the density fluctuations, is modeled as

$$m(t) = v_1\phi(t) + v_2\phi^2(t). \tag{2}$$

Here, $v_1 \geqslant 0$ and $v_2 \geqslant 0$ are the coupling coefficients. The state of the system is specified by a point $\mathbf{V} = (v_1, v_2)$ in the v_1-v_2 plane. For small $\mathbf{V}$, the model describes liquid states where $\phi(t\to\infty) = 0$. For large $\mathbf{V}$, one gets a nontrivial long-time limit $f = \phi(t\to\infty)$, $0 < f < 1$. Parameter f quantifies the arrest of density fluctuations in the non-ergodic glass state. There are lines of liquid-glass transition points $\mathbf{V}^c = (v_1^c, v_2^c)$,

each characterized by some number λ, $1/2 \leqslant \lambda < 1$. This number determines the critical exponent a, $0 < a < 1/2$, and the von Schweidler exponent b, $0 < b \leqslant 1$, by the relation $\Gamma(1-a)^2/\Gamma(1-2a) = \lambda = \Gamma(1+b)^2/\Gamma(1+2b)$. We consider the line, which can be parameterized by $v_1^c = (2\lambda - 1)/\lambda^2$, $v_2^c = 1/\lambda^2$, $0.5 \leqslant \lambda < 1$. Crossing the line, the long-time limit of $\phi(t)$ jumps from zero to the critical value $f^c = 1 - \lambda$. The distance of the state $\mathbf{V}$ from $\mathbf{V}^c$ is specified by the separation parameter $\sigma = [(v_1 - v_1^c) + (v_2 - v_2^c)f^c]f^c(1 - f^c)$, which is negative for liquid states and positive for glass states. This model is the simplest one reproducing all values for the anomalous exponents, which can occur in the general theory [13]. The parameter f^c appears as plateau value of the $\phi(t)$-versus-$\log t$ curves for $\mathbf{V}$ near $\mathbf{V}^c$ or as relative strength of the α-peak of the loss spectrum [7].

The probing-variable correlator $\phi_A(t)$ obeys the same general equation of motion and initial decay as $\phi(t)$, but Ω, v and $m(t)$ have to be replaced by the corresponding quantities Ω_A, v_A and $m_A(t)$. The model for the kernel is

$$m_A(t) = v_A \phi(t) \phi_A(t), \tag{3}$$

where $v_A > 0$ quantifies the coupling of the probing variable to the density fluctuations. If $v_A f^c > 1$, the long-time limit of $\phi_A(t)$ jumps from zero to the critical value $f_A^c = 1 - 1/(v_A f^c)$ as $\mathbf{V}$ crosses the transition line. Originally, this model was motivated for the density fluctuations of a tagged particle [14]. Also, the MCT equations for reorientational dynamics of a linear molecule suggest an expression like Eq. (3) [15]. Within the microscopic theory, the coupling coefficients depend on the equilibrium structure functions, which depend smoothly on T. Therefore, v_1, v_2, and v_A are smooth functions of the temperature. The specified model was applied repeatedly for the description of experiments, as can be inferred from Ref. [16] and the papers cited there.

The long-time decay of the correlators at the transition point is given by $[\phi(t) - f^c]/h = [\phi_A(t) - f_A^c]/h_A = (t_0/t)^a + O(t^{-2a})$. The time t_0 depends on the transient dynamics. It is determined by matching the numerical solution of $\phi(t)$ for large times to the asymptotic formula. The amplitudes are $h = \lambda$, $h_A = \lambda/(v_A f^{c\,2})$. In the limit of small $|\sigma|$, there appears a large time interval where $|\phi(t) - f^c|$ is small. Here, one gets in leading-order $[\phi(t) - f^c]/h = [\phi_A(t) - f_A^c]/h_A = c_\sigma g(t/t_\sigma)$. This is a scaling law with a correlation scale $c_\sigma = \sqrt{|\sigma|}$ and a time scale $t_\sigma = t_0/|\sigma|^{1/2a}$. The function $g(\hat{t})$ is determined solely by λ. It exhibits the critical power law for small rescaled times $\hat{t}$, $g(\hat{t} \ll 1) = 1/\hat{t}^a$, and von Schweidler's power law for large rescaled times in the liquid, $g(\hat{t} \gg 1) = -B\hat{t}^b$ [7]. The scaling law implies one for the response functions

$$\chi(t)/h = \chi_A(t)/h_A = s_\sigma k(t/t_\sigma), \tag{4}$$

where $s_\sigma = c_\sigma/t_\sigma$. The master function $k(\hat{t}) = -\partial \hat{g}/\partial \hat{t}$ interpolates between the critical power law, $k(\hat{t} \ll 1) = -a/\hat{t}^{(1+a)}$, and, in the liquid state, the von Schweidler power law, $k(\hat{t} \gg 1) = -bB/\hat{t}^{(1-b)}$.

The VH-light-scattering spectra of Salol [3] or orthoterphenyl [17] show that f_A^c is about 0.9. This means there is strong arrest of the reorientational motion at the ideal glass-transition points in these van-der-Waals systems. Integrating $\chi_A(t)$ over time, one can determine $\phi_A(t)$ and read off the plateau. We find $f_A^c = 0.90 \pm 0.05$ from the $T = 260$K-data for BZP [5] and $f_A^c = 0.93 \pm 0.03$ from those for Salol at $T = 257$K [2], corroborating the preceding conclusion. Therefore, we focus on $\chi_A(t)$ for large translation-rotation coupling v_A.
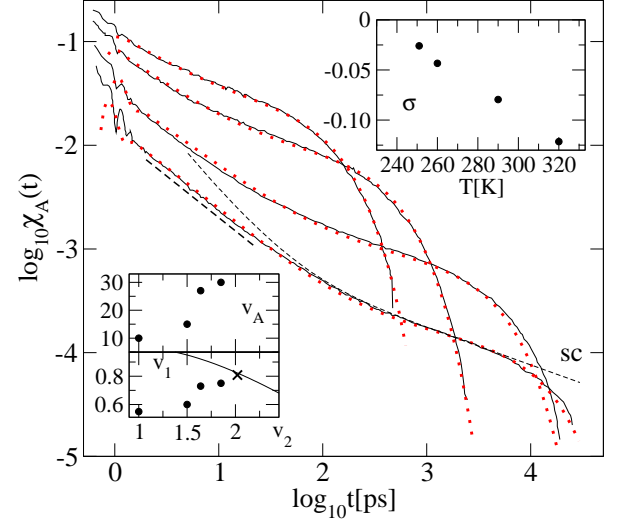

FIG. 1: OKE response $\chi_A(t)$ measured for BZP for temperatures $T/\text{K} = 251, 260, 290, 320$ (full lines from bottom to top) [5]. The dashed straight line has slope $x = 0.80$. The dotted lines exhibit results $N \cdot \chi_A(t)$, with $\chi_A(t)$ calculated for the MCT model defined by Eqs. (1–3) with $\Omega = \Omega_A = 0.2v = 0.2v_A$. The factors N and Ω are chosen (from bottom to top) as 3.5, 6, 9.5, 8, and 1.67, 1.43, 2.0, 2.0 THz, respectively. The left inset exhibits the variation of the coupling constants with changes of the temperature, and the right inset the one of the separation parameter σ. The dashed line marked sc shows a scaling-law result, Eq. (4), calculated for $\lambda = 0.70$. The line in the lower left inset exhibits transition points $\mathbf{V}^c$; the point $\sigma = -0.003$ for $\lambda = 0.70$, is marked by a cross.

Figure 1 reproduces the OKE response functions for BZP [5]. A dashed straight line of slope $x = 0.80$ shows that the data for $T = 251$ K exhibit power-law decay $\chi(t) \propto 1/t^x$ for 2 ps $\leqslant t \leqslant 20$ ps. There is a von Schweidler-law-like variation: $\phi(t) - \text{const.} \propto -t^{b'}$, $b' = 1 - x = 0.20$. In the double-logarithmic representation, the scaling-law result, Eq. (4), appears as interpolation between a straight line of slope $(1+a) > 1$, and one of slope $(1-b) < 1$. Changing the scales $s_\sigma h_A$ and t_σ is equivalent to a translation of the curve. The dashed line marked sc shows an example calculated for $\lambda = 0.70$ ($a = 0.33$, $b = 0.64$) shifted to match the data for $T = 251$ K. It provides a proper description of the observations for 60 ps $< t <$ 6 ns. However, since $1 + a > 1 > x$, the scaling law cannot account for the data for $t < 60$ ps. This conclusion [5] is not altered by choosing λ or t_σ, s_σ differently. The dots are the theoretical results for $\chi_A(t)$ scaled by

amplitude factors N and scales Ω, which vary somewhat with T. Notice that the calculated functions exhibit transient oscillations for times below and up to 2 ps, as do the measured curves. This shows that the parameters Ω, ν, Ω_A, ν_A are chosen reasonably. The strong variation of $\chi_A(t)$ with changes of T is due to the changes of the coupling coefficients as documented in the left inset. The state $\mathbf{V} = (\nu_1, \nu_2)$ shifts towards the transition line if T decreases. An extrapolation to a transition point for $\lambda = 0.70$, which is near the cross, is consistent with the fit values for ν_1 and ν_2. Parameter σ exhibits an almost linear temperature dependence, and extrapolation to $\sigma = 0$ suggests $T_c \approx 235$ K. Uncertainty estimates for λ and T_c cannot be given yet, since we did not study in detail the possibility for data fits by other choices for ν_1, ν_2, and ν_A.
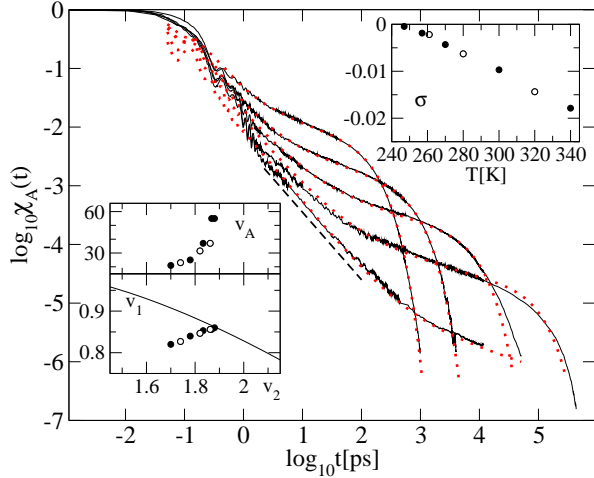
FIG. 2: Analog results as the ones in Fig. 1 for data measured for Salol for $T/\mathrm{K} = 247, 257, 270, 300, 340$ [2]. The dashed straight line has slope x=1.15. The MCT results are calculated for 7.9 THz $= \Omega = 2\Omega_A = 10\nu_A$, $\nu = 0$, and factors $N = 25, 37.3, 27.8, 17.9, 19$, respectively. The open circles in the insets are the fit values for the other measured temperatures [2]; the corresponding response functions are not shown to avoid overloading.

Figure 2 shows the OKE response for Salol for the highest and lowest temperature measured and three temperatures in between [2]. The data are normalized to unity for $t = 0.01$ ps. A dashed straight line of slope $x = 1.15$ shows that the data for $T = 247$ K can be described by $\chi(t) \propto 1/t^x$ for the interval 2 ps $< t <$ 100 ps. Equivalently, the correlator shows a decay similar to the critical one, $\phi(t) \propto 1/t^{a'}$ with $a' = x - 1 = 0.15$. For the $T = 257$ K data, a similar behavior is found with $x \approx 0$, i.e., $\phi(t)$ exhibits logarithmic decay [2]. The MCT fits have been evaluated for temperature-independent parameters Ω, Ω_A, ν, ν_A. The normalization constants N exhibit some T dependence. The path $\mathbf{V} = (\nu_1, \nu_2)$ extrapolates to a critical point for $\lambda = 0.73$ ($a = 0.31$, $b = 0.59$). The σ-versus-T results suggest $T_c \approx 245$ K. The numbers for λ and T_c are consistent with those obtained previously [1, 2, 3, 4]. For the identification of the ideal transition point it would be helpful to have data available also for T below the estimated T_c. The variation of ν_A closely follows an Arrhenius law: $\nu_A \propto \exp(T_0/T)$,

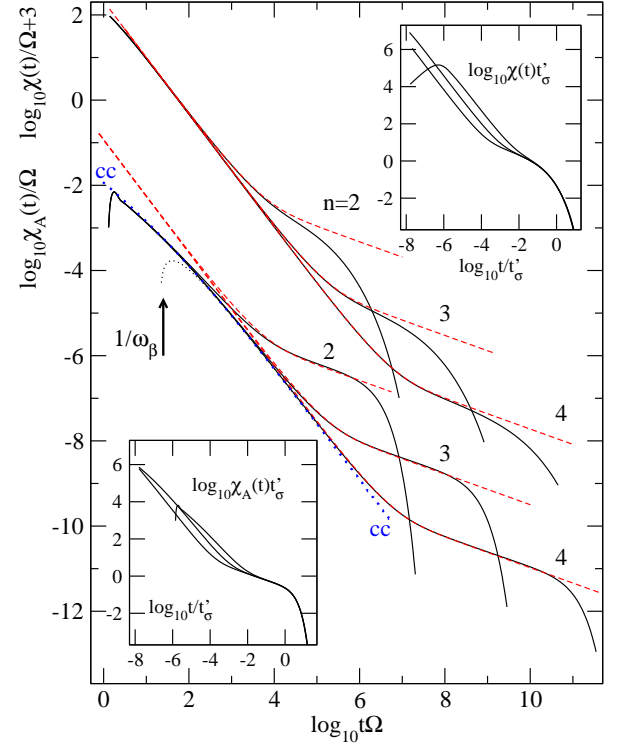where the fit value $T_0 = 1000$ K is not unreasonable for a van-der-Waals liquid.

FIG. 3: Response functions for the model defined by Eqs. (1–3) calculated with $\Omega = \Omega_A = \nu/5 = \nu_A/5$ and $\nu_A = 20$ for three states specified by $\lambda = 0.70$, $(\nu_1, \nu_2) = (\nu_1^c, \nu_2^c)(1 + \varepsilon)$, $\varepsilon = -10^{-n}$, $n = 2, 3, 4$, yielding $\sigma = 3\varepsilon/10$. The results for $\chi(t)$ are shifted upwards by 3 decades. The dashed lines are the scaling-law results, Eq. (4), where $t_0 = 0.755$. The dotted line shows the leading correction to the scaling-law for short times. The dotted line marked cc exhibits the Cole-Cole response function $\chi_A^{cc}(t)$. The insets demonstrate the superposition principle for the long-time dynamics.

Figure 3 shows the two response functions, $\chi(t) = -\partial\phi(t)/\partial t$ and $\chi_A(t) = -\partial\phi_A(t)/\partial t$, for three liquid states near the transition point with $\lambda = 0.70$ and the corresponding scaling-law results. There is a second scaling law, the superposition principle for the α process, dealing with the dynamics for times within the von Schweidler-law regime and longer: $\chi(t) = \tilde{\chi}(t/t_\sigma')/t_\sigma'$, $\chi_A(t) = \tilde{\chi}_A(t/t_\sigma')/t_\sigma'$, $t_\sigma' = t_0/|\sigma|^\gamma$, $\gamma = 1/(2a) + 1/(2b)$. The insets demonstrate this result. The solution at $\mathbf{V}^c$ including the leading correction reads $[\phi_A(t) - f_A^c] = h_A(t_0/t)^a[1 + K_A(t_0/t)^a]$ and a corresponding formula with index A dropped. The number $K_A = -1.5$ is evaluated from the coupling constants ν_1, ν_2, ν_A; it is negative and large since f_A^c is high [7]. The result is shown as dotted line for χ_A. The corresponding correction for $\chi(t)$, $K = 0.020$, is so small that it cannot be made visible in Fig. 3. This exemplifies that the range of validity of the universal formulas can be quite different for different functions. The scaling-law formulas explain quantitatively the evolution of the glassy dynamics as exhibited by $\chi(t)$ and this for the complete regime outside the transient, $\Omega t > 2$. The state $n = 2$ is marked by

a cross in the left inset of Fig. 1. The states of interest for the data interpretation have a much larger separation from the critical point. One finds here, as in previous work [7, 16], that the scaling-law description can explain all the qualitative features of $\chi(t)$, but that a quantitative description does not work for $|\sigma| > 0.05$. The same conclusions are valid for $\chi_A(t)$, albeit only for times with $t\Omega \gtrsim 3000$. The size of the correction term K_A is so large, that there appears a three-decade time interval outside the transient where the universal formulas cannot account for the MCT solution. Within the interval $2 \leqslant \log_{10}(\Omega t) \leqslant 3.5$, the leading-order-correction formula describes the results. But for $0.5 \leqslant \log_{10}(\Omega t) \leqslant 2$, even this formula is insufficient. Within the interval $0.5 \leqslant \log_{10}(\Omega t) \leqslant 3.5$, nearly-logarithmic decay is exhibited by $\phi_A(t)$.

The equation of motion for $\phi_A(t)$ is equivalent to $\chi_A(\omega) = -\Omega_A^2/[\omega(\omega + i\nu_A) - \Omega_A^2 + \Omega_A\omega \, m_A(\omega)]$, where $\chi_A(\omega)$ and $m_A(\omega)$ are the Fourier transforms of $\chi_A(t)$ and $m_A(t)$, respectively, for frequency ω. For low-frequency phenomena, $|\omega(\omega + i\nu_A)| \ll \Omega_A^2$, this simplifies to $\chi_A(\omega) = 1/[1 - \omega \, m_A(\omega)]$. For $t/t_0 \gg 1$ and $t/t_\sigma \ll 1$, one gets up to next-to-leading order: $m_A(t) = f_m + h_m(t_0/t)^a[1 + K_m(t_0/t)^a]$, where $f_m = \nu_A f^c f_A^c$, $h_m = \nu_A(f^c h_A + f_A^c h)$, $K_m h_m = \nu_A[f^c h_A K_A + f_A^c h K + h h_A]$. There is a trend that the negative contribution of the first term in the bracket is canceled by the positive one due to the last term. Hence, because the correction term K_A for $\phi_A(t)$ is large, the correction term $K_m = 0.16$ for $m_A(t)$ is small. Thus, the critical law is a good approximation for $m_A(t)$. This leads to the Cole-Cole formula for the β-process: $\chi_A^{cc}(\omega) = \chi_0^{cc}/[1 + (-i\omega/\omega_\beta)^a]$, $\chi_0^{cc} = 1/[1 + f^c f_A^c \nu_A]$, $\omega_\beta = [(1 + f_m)/h_m\Gamma(1-a)]^{1/a}/t_0$. The limit $\omega/\omega_\beta \ll 1$ reproduces the universal critical decay: $\chi(t) \propto 1/t^{1+a}$. The limit $\omega/\omega_\beta \gg 1$ leads to a von Schweidler-law-like decay: $\chi(t) \propto 1/t^{1-a}$. It depends on the relative size of t_0^{-1}, ω_β and t_σ^{-1}, which part of the β-peak spectrum dominates the nearly-logarithmic decay, $\chi(t) \propto 1/t^x$, $1 - a \leqslant x \leqslant 1 + a$. The dotted line in Fig. 3 marked cc exhibits $\chi_A^{cc}(t)$ for our model. The preceding reasoning for using the leading asymptotic expansion for $m_A(t)$ rather than for $\phi_A(t)$ is valid also for the microscopic version of MCT. The schematic model used here is merely the simplest example illustrating our derivation of the β-peak phenomenon.

We have shown that the evolution of glassy dynamics as measured by OKE spectroscopy for two liquids can be described reasonably by the solutions of a standard schematic MCT model, and this for time intervals extending up to five orders of magnitude. The long-time part of the response functions can be explained qualitatively by the known scaling laws reflecting leading-order asymptotic solutions of the MCT

equations. The leading-order correction formulas explain that for strong probing-variable-environment coupling there appears a large time interval adjacent to the one for the transient motion where the scaling laws cannot explain the data. The nearly-logarithmic decay within this interval is explained as β-peak dynamics and is fitted perfectly by the solutions of the schematic model. Our theory implies the prediction of nearly-logarithmic decay of reorientational correlations for liquids of molecules with large elongation. Molecular-dynamics simulations can test this and provide the structure factors for a microscopic calculation within MCT. Such work could substantiate or falsify the preceding explanation. It remains to be explained why the β-peak phenomenon has not been detected in earlier studies.

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